Available online at www.sciencedirect.com

ScienceDirect

Pacific Science Review 16 (2014) 183–188

www.elsevier.com/locate/pscr

Novel hydrodynamic instability of the molten Au/Pd alloy film irradiated by tightly focused femtosecond laser pulses

Alexander A. Kuchmizhak [a,*], Oleg B. Vitrik [a,b], Yuri N. Kulchin [a,b]

[a] *Institute of Automation and Control Processes, Vladivostok, Russia*
[b] *Far Eastern Federal University, Vladivostok, Russia*

Received 9 December 2014; accepted 6 February 2015
Available online 17 March 2015

Abstract

Features of nanoscale surface hydrodynamic instabilities induced on the thin Au/Pd alloy films by single femtosecond pulses shaped into the tightly focused quasi-Bessel beam by means of a fiber microaxicon were studied. The thickness of the metal film as well as the pulse energy were found to be the key parameters determined the types of the hydrodynamic instability of the molten film, which results in the formation of different frozen surface relief microstructures: nanojets, nanocrowns and hybrid structures. Single nanojets forms on the surface of the 80-nm-thick film at the pulse energies ranging from 6 to 7 nJ, while for thicker films formation of hybrid structure, a nanojet surrounded by the nanocrown, is observed. Single nanocrown can be fabricated at film thicknesses ranging from 120 to 240 nm at near-threshold pulse energies. The number of nanospikes of the nanocrown was found to be linearly dependent on the pulse energy and the inverse film thickness.

Keywords: Laser-assisted nanostructuring; Femtosecond pulses; Fiber microaxicon; Molten film; Hydrodynamic instability

Introduction

Laser-driven instability of a molten metal film surface under the action of tightly focused single nano-, pico- and femtosecond laser pulses leads to the formation of a variety of unique sub-micron surface structures [1–4]. Among such laser-induced microstructures nanojet (also referred to as nano-waterdrops), a single standing sharp spike of the molten material with a submicron particle atop, and nanocrown representing a set of sharp nanosized spikes with the sub-100 nm nanoparticles atop [4] periodically placed along the interface of the molten and unmodified metal film attract the great researcher's attention. These structures show a local electromagnetic fields enhancement [5], resonant optical absorption [6], enhanced photoemission [6], etc. Unique properties along with the versatility, high efficiency and low cost of laser "up-down" fabrication techniques make these structures very promising candidates for practical application as optical nanoantennas for manipulation of the electromagnetic fields at

* Corresponding author.
E-mail address: ku4mijak@dvo.ru (A.A. Kuchmizhak).
Peer review under responsibility of Far Eastern Federal University, Kangnam University, Dalian University of Technology, Kokushikan University.

http://dx.doi.org/10.1016/j.pscr.2015.02.005

nanoscale, sensitive elements in the plasmonic refractive index sensors, the functional elements of micro- and nanoelectronics vacuum devices for enhanced electron yield, substrates for SERS signal amplification, etc. It is noteworthy that the geometric shape of the frozen laser-driven instabilities (nanojets and nanocrowns) resembles the impact of the falling water drop on the water or other liquid surface detected by using the high-speed camera [7], which presumably indicates the similarity of the formation mechanisms occurring both in the aqueous layer and the molten metal film heated by the focused ultrashort laser pulse. While the particular instability type in the aqueous layer is determined by the physical properties and the thickness of this layer, ambient conditions, impact velocity and drop size, the nanojets and nanocrowns formation under the action of focused laser pulses is determined by the properties and the thickness of the metal film, pulse energy, as well as the focal spot size [1–8]. Nevertheless, by varying these experimental parameters so far only two types of laser-driven surface instabilities of the melt metal film were experimentally obtained, while a number of experiments in fluid dynamics demonstrate the formation of more complex types of instabilities (Pelegrine Sheet, Crown Splash, Microdroplet Splash, as well as their intermediate cases) pointing out the possibility to obtain novel laser-induced structures with new unique properties.

In this paper, we experimentally demonstrate for the first time that the irradiation of the Au/Pd alloy film by single tightly focused femtosecond pulses under appropriate experimental conditions leads to the a novel laser-induced instability of the molten metal film, which results in the formation of a hybrid microstructure resembling both the nanojet and the nanocrown. In this paper we will show that the thickness of the metal film along with the pulse energy are the key parameter determined the type of obtained laser-induced nanostructures. Underlying mechanisms responsible for the formation of these laser-induced nanostructures are also discussed in this paper.

Experimental details

In our experiments to create a laser-induced instabilities of the surface relief of the metal film, the second harmonic ($\lambda = 400$ nm) of a commercial femtosecond laser system (Tsunami Femtosecond Oscillator and Spitfire Amplifier, Spectra Physics) generated 80-fs pulses with a maximal frequency up to 1 kHz is used. Thin Au/Pd films (wt. 80/20%) of variable thickness (80, 120, 160 and 250 nm) were deposited on the smooth cleaved fiber endface by magnetron sputtering with the average deposition rate ~ 0.17 nm/s. Laser pulses were focused on the Au/Pd film surface by a fiber microaxicon (FMA) made on the flat endface of the 5-mm long section of the commercial optical fiber (optical core diameter ~ 1.5 μm) by using a modified chemical etching [9].

FMA's geometric parameters (full cone angle $\theta \approx 110^\circ$ and the cone base diameter $D = 2$ μm, (Fig. 1(b)) were optimized to provide tightly focused laser spot with lateral FWHM diameter ~ λ and the focus depth ~3.5 λ at $\lambda = 400$ nm, thus ensuring the ability to move the FMA during the laser modification process at a distance from the metal film surface sufficient for unobstructed growth of the nanojets and nanocrowns (in our experiments, maximal nanojet's height does not exceed 1 μm). The laser spot at the FMA output represents a central symmetrical quasi-Bessel beam (Fig. 1(c)), surrounded by an additional low-intensity maximum, which is not involved in the laser modification process. The sample was placed on a linear motorized nanopositioners system (Newport XM series), which provides a 50-nm movement precision along three axes. The FMA is placed perpendicularly to the metal film surface, while the probe-to-sample distance (in this case ~ 3 λ) was maintained at a constant level using a tuning fork feedback system. All laser-induced structures were fabricated by single-pulse irradiation under ambient conditions and post-characterized using scanning electron microscope (SEM, Hitachi S3400N).

Results and discussions

The result of the single femtosecond pulse impact on the 80-nm-thick Au/Pd film is demonstrated in Fig. 3 for different pulse energies E. The visible modification of the metal film by a femtosecond pulse occurs at the pulse energy ~3 nJ representing a molten area with recrystallization grains of metal nanocrystallites.

The lateral size of the molten area (~600–700 nm) is about half times larger than the initial optical spot (~410 nm) on the film surface, which presumably indicates the sufficient lateral heat transfer during the heated laser pulse. Note that significant exfoliation of the metal film on the glass substrate at these pulse energies is not observed. However, at further pulse energy increase up to 6 nJ the microbump structure is formed, with the molten material being tended to concentrate mainly at the forming frozen standing

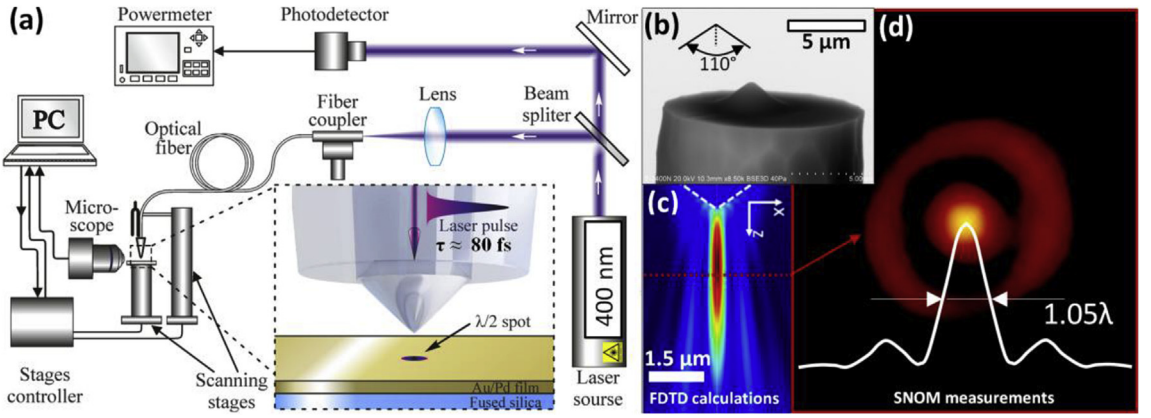

Fig. 1. (a) Schematic of the experimental setup. (b) SEM image of the fiber microaxicon used. (c) Laser intensity map at the microaxicon output illustrating the quasi-Bessel beam generation with the focal depth ~3.5 λ. (d) Transverse power distributions (λ = 405 nm) at the FMA focal plane experimentally measured using aperture-type SNOM probe with its central cross-section being showed by white curve (FWHM diameter of the central spot is about λ, which is also in good agreement with the FDTD calculations made).

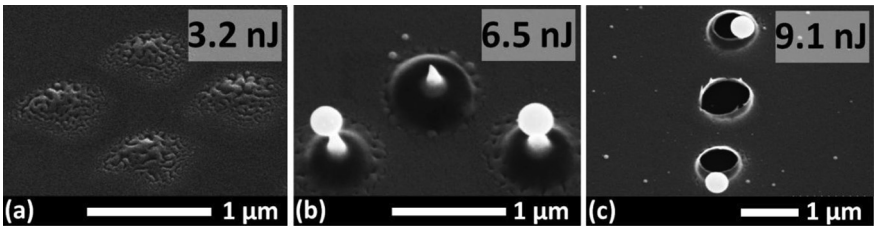

Fig. 2. Side-view SEM images of main types of laser-induced microstructures fabricated on the 80-nm-thick Au/Pd film irradiated by single femtosecond pulses at pulse energies E = 3.2 nJ (a), 6.5 nJ (b), and 9.1 nJ (c).

nanojet. The height of this nanojet can reach ~500–700 nm, with spherical nanoparticles being remained atop or detached under certain conditions. Formation of the nanojet under the femtosecond pulses irradiation refers to the thermocapillary instability of the molten metal film. The formation mechanism of such a submicron structure, actively discussed recently in the literature, is associated with a number of reasons: Marangoni convection flow [1] accumulating the molten film at the center of the optical spot with

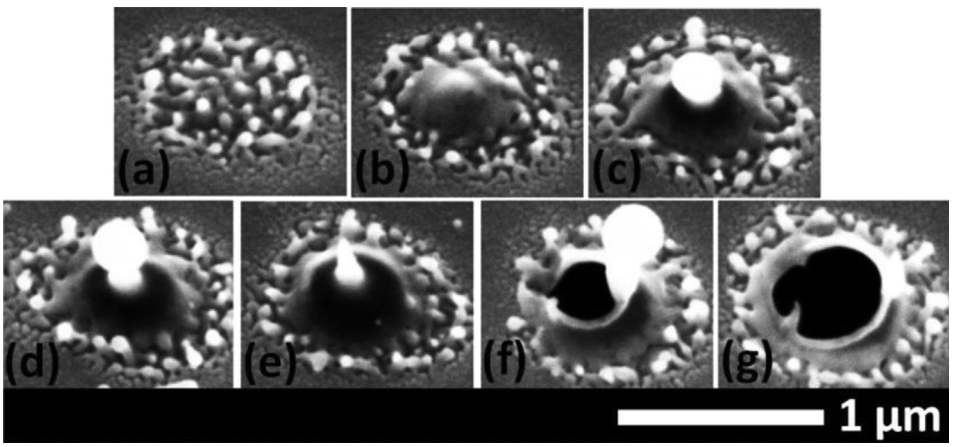

Fig. 3. Side-view SEM images of main types of laser-induced microstructures fabricated on a 120-nm-thick Au/Pd film irradiated by single-pulse irradiation at the pulse energies E = 5.8 nJ (a), 6.2 nJ (b), 7 nJ (c), 7.5 nJ (d), 8.1 nJ (e), 9.5 nJ (f), 10 nJ (g).

maximal intensity [4], vapor recoil pressure [10], thermoelastic and plastic deformations that occur during heating of the film [1], etc. The spherical nanoparticle detaching from the nanojet occurs owing to the hydrodynamic Rayleigh-Plateau instability [1].

Note that, thermocapillary instability leading to the nanojet formation has been demonstrated only for pure Au films [1–6], while the jetting behavior of the Au/Pd alloy films has been shown only recently [11]. At further pulse energy increase (E ≈ 10 nJ) the microbump with the nanojet collapses forming the 400-nm-wide through hole and the spherical nanoparticles. Such jetting behavior of the Au/Pd film indicates the similarity of the formation mechanisms with the pure Au.

Nanojets formation is also observed at the surface of the 120-nm-thick Au/Pd film as for the case of thicker film. However, on the boundary of the protrusion surrounding the nanojet and unmodified metal film, the molten film demonstrates a periodic modulation of the height with the total number of the nanoscale protrusions up to 25 (Fig. 3(a,b)). This feature is also observed at higher pulse energies, at which the microbump supported the nanojet is collapses forming the 350-nm-wide through hole with the upright standing nanojet (Fig. 3(c–f)). It should be noted that the individual "crown-like" hydrodynamic instability resulting in the formation of nanocrowns without the central nanojet was first demonstrated in [4] using femtosecond-, and very recently, nanosecond laser pulses [10]. However, the formation of nanojet surrounded by the nanocrown has been reported for the first time.

Presence of the crown-like thermocapilar instability of the molten melt film more clearly seen at 160-nm and 250-nm-thick Au/Pd films at the initial stages of their laser-induced modifications (see. Fig. 4(a) and (g)). Thus, the impact of the single femtosecond pulse at E = 5 nJ leads to the formation of annular rim resembling the initial stage of crown. It is noteworthy that at these pulse energies the central part of the molten rim at the point with maximal intensity of the Bessel beam, remains almost unmodified. As seen from the SEM images of the laser-induced surface instabilities obtained for different Au/Pd film thicknesses, the crown-like instability becomes more pronounced at increasing film thickness, while the central nanojet decreases in size. It also should be noted that the average number of the nanospikes of the surrounded crown-like microstructure N decreases from 25 for 120-nm-thick Au/Pd film to ~13 for twice thicker film, resulting in almost linear dependence of N on the film thickness d (Fig. 5). This result is in good quantitative agreement with the recently developed theoretical model of the nanocrowns formation based on a hydrodynamic surface instability and described by a Kuramoto-Sivashinsky equation, which predicts linear dependence of the nanospikes number on the film thickness [12].

$$N = \frac{3R_m}{2d}\left[\frac{|\sigma_T||\partial T/\partial z|_d d}{\sigma}\right]^{1/2}$$

where R_m is the nanocrown radius, $\sigma_T = \partial\sigma/\partial T$ and $\partial T/\partial z$ are the normal temperature gradient in the nanocrown wall and the surface tension temperature gradient, respectively. In addition, for a given film thickness, N is slightly increases with the pulse energy E (Fig. 5), which also does not contradict with the developed model [12].

The formation mechanism of the fabricated laser-induced microstructures seems to be determined by the hydrodynamic properties of the molten Au/Pd alloy film. SEM images of the frozen nanojets and nanocrowns clearly indicate the presence of the material in the liquid phase. Nevertheless, the observation of the "dual" hydrodynamic instability appeared through a complex microstructure consisted from both the nanojet and the nanocrown, evidently indicates the presence of at least two opposite flows of the molten metal film. In general, this two flow directions were already described separately in the literature, [1,3,4,12].

Under the action of tightly focused 160-fs pulse with the quasi-Bessel spatial energy distribution the Au/Pd film becomes liquid. The surface tension gradient caused by the nonuniform temperature profile pulls the molten material ($d\sigma/dT < 0$) from a heated area, which coincides with the optical spot, to a less heated periphery [12]. This feature is clearly observed for the Au/Pd films with the thicknesses ranging from 120 to 240 nm at the initial low-energy stage of their surface modification, which substantially represents 1-μm-wide melt rim with periodically modulated height and significantly less affected central part (see Fig. 4(a)–(g)). Friction forces in the melt layer are increased versus its radially decreasing depth, slowing down the outward melt motion and eventually stopping it at the melt-solid boundary, where the thermocapillary or cavitation pressure pushes it to move up along the surface normal, forming sharp nanospikes circumferentially spaced along the molten rim [12]. Hydrodynamic instability of the molten film, resulting in a periodic modulation of the nanospikes, is determined

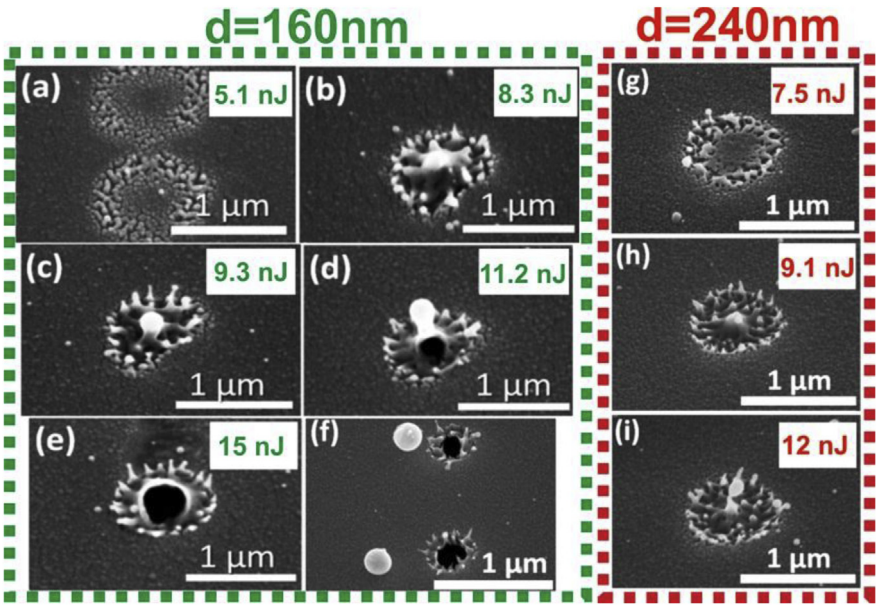

Fig. 4. Side-view SEM images of main types of laser-induced microstructures fabricated on a 160-nm (left column) and 250-nm (right column)-thick Au/Pd film.

by the temperature gradient ($d\sigma/dz$) of the melt rim as well as by the change of the surface tension gradient due to the height modulation of the molten rim. Increase of the Au/Pd film thickness d at the corresponding growth of the pulse energy E, apparently leads to the transfer of the increasing volume of molten material from the central area resulting in the growth of more pronounced nanocrowns for thicker Au/Pd films.

We also note that, in accordance with the findings of [12], the formation and complete solidification of the nanocrown occur at the characteristic times ~10–20 ns. At such times, the central area of the molten pool clutched by the solidified nanocrown remains liquid due to the low thermal conductivity of the glass substrate. At the certain threshold energy determined by the film thickness d, as it was experimentally shown in this paper, the central part of the molten pool breaks away from the glass substrate. Exfoliation of the metal film and the glass substrate along the surface normal can occur due to increased vapor recoil pressure, subsurface boiling at the film–substrate interface, plastic deformation of the metal film, as well as the complex combination of these mechanisms. Exfoliation of the metal film from the substrate leads to changes of the temperature gradient of the surface tension ($d\sigma/dT > 0$), resulting in the accumulation of the molten material in the form of the sharp spike as well as thinning of the surrounding microbump, which can be clearly seen from the noticeable darkening of the area around the nanojet (Figs. 2(b) and 3(d,e)). Ascending flows of the molten material form a spherical mesoparticle at the nanojet tip, which can remain atop or detach it.

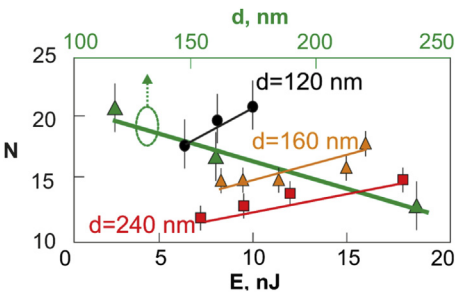

Fig. 5. Average number of nanospikes in the nanocrown N as a function of the film thickness d (upper axis) and pulse energy E obtained at d = 120, 160 and 240 nm.

Conclusions

In conclusion, features of nanoscale surface hydrodynamic instabilities induced on the thin Au/Pd alloy films by single femtosecond pulses shaped into the tightly focused quasi-Bessel beam by means of a fiber microaxicon were studied. The thickness of the metal film as well as the pulse energy were found to be the key parameters determined the types of the hydrodynamic instability of the molten film, which results in the formation of different frozen surface relief

microstructures: nanojets, nanocrowns and hybrid structures. Single nanojets forms on the surface of the 80-nm-thick film at the pulse energies ranging from 6 to 7 nJ, while for thicker films formation of hybrid structure, a nanojet surrounded by the nanocrown, is observed. Single nanocrown can be fabricated at film thicknesses ranging from 120 to 240 nm at near-threshold pulse energies. The number of nanospikes of the nanocrown was found to be linearly dependent on the pulse energy and the inverse film thickness. We believe, that more comprehensive studies of the laser-driven instabilities of the molten metal films opens up new prospects for creation of cheap "up-down" laser technology of nanostructure fabrication for nanophotonics, plasmonics, SERS experiment, etc.

Acknowledgments

Authors are grateful for partial support from the Russian Foundation for Basic Research (Projects nos. 14-02-31323-mol_a, and 14-29-07203-ofi_m). The project was also financially supported by the Russia Federation Ministry of Science and Education, Contract No 02.G25.31.0116 of 14.08.2014 between Open Joint Stock Company "Ship Repair Center "Dalzavod" and RF Ministry of Science and Education.

References

[1] J. Koch, et al., Nanotexturing of gold films by femtosecond laser-induced melt dynamics, Appl. Phys. A 81 (2005) 325−328.

[2] J.P. Moening, et al., Formation of high-aspect-ratio protrusions on gold films by localized pulsed laser irradiation, Appl. Phys. A 95 (2009) 635−638.

[3] Y. Nakata, et al., Solid-liquid-solid process for forming free-standing gold nanowhisker superlattice by interfering femtosecond laser irradiation, Appl. Surf. Sci. 274 (2013) 27−32.

[4] Y. Nakata, et al., Liquidly process in femtosecond laser processing, Appl. Surf. Sci. 255 (2009) 9761.

[5] M. Reininghaus, et al., Fabrication and spectral tuning of standing gold infrared antennas using single fs-laser pulses, Opt. Express 31 (2013) 32176.

[6] J.P. Moening, et al., Field-emission properties of sharp high-aspect-ratio gold cones formed via single pulse laser irradiation, Appl. Phys. A 100 (2010) 1013−1017.

[7] D.T. Papageorgiou, On the breakup of viscous liquid threads, Phys. Fluids 7 (1995) 1529.

[8] A.A. Kuchmizhak, et al., Fabrication of porous metal nanoparticles and microbumps by means of nanosecond laser pulses focused through the fiber microaxicon, Opt. Express 22 (2014) 19149−19156.

[9] A.A. Kuchmizhak, et al., High-quality fiber microaxicons fabricated by a modified chemical etching method for laser focusing and generation of Bessel-like beams, Appl. Opt. 53 (2014) 937−943.

[10] Y.N. Kulchin, et al., Through nanohole formation in thin metallic film by single nanosecond laser pulses using optical dielectric apertureless probe, Opt. Lett. 38 (2013) 1452−1454.

[11] V.I. Emel'yanov, et al., Nanoscale hydrodynamic instability in a molten thin gold film induced by femtosecond laser ablation, JETP Lett. 99 (2014) 518−522.

[12] Y.N. Kulchin, et al., Formation of crown-like and related nanostructures on a thin supported gold film irradiated by single diffraction-limited nanosecond laser pulses, Phys. Rev. E 90 (2014) art. No. 023017.